CLAIMS

1. A production method for an organic-silica complex membrane having a sulfonic acid group, being characterized by comprising the steps of:

obtaining a sulfonic acid derivative by allowing an alkoxysilane compound having an amino group to react with a cyclic sultone; and

subjecting the sulfonic acid derivative to a condensation reaction.

2. A production method for an organic-silica complex membrane having a sulfonic acid group, being characterized by comprising the steps of:

obtaining a sulfonic acid derivative by allowing a secondary or tertiary amine derivative which is obtained by allowing an alkoxysilane compound having an amino group to react with a compound having at least 2 epoxy groups in a molecule to react with a cyclic sultone; and

subjecting the sulfonic acid derivative to a condensation reaction.

3. A production method for an organic-silica complex membrane having a sulfonic acid group, being characterized by comprising the steps of:

obtaining a sulfonic acid derivative by allowing a secondary or tertiary amine derivative which is obtained by

allowing an alkoxysilane compound having an epoxy group to react with an amine compound having at least 2 amine valences (number of hydrogen atoms originated in an amino group contained in one molecule) to react with a cyclic sultone; and

subjecting the sulfonic acid derivative to a condensation reaction.

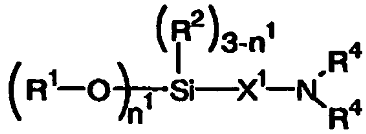
4. A production method for an organic-silica complex membrane having a sulfonic acid group, being characterized by comprising the steps of:

obtaining a sulfonic acid derivative by allowing a secondary or tertiary amine derivative which is obtained by allowing an alkoxysilane compound having an amino group to react with an alkoxysilane compound having an epoxy group to react with a cyclic sultone; and

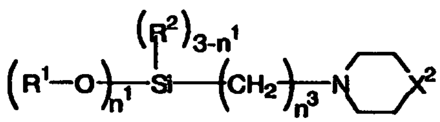
subjecting the sulfonic acid derivative to a condensation reaction.

5. The production method as set forth in Claim 1, 2 or 4, wherein the alkoxysilane compound having an amino group is represented by the following general formulae (1) to (5):

$$\left(R^1-O\right)_{n^1}\overset{\left(R^2\right)_{3-n^1}}{\overset{|}{Si}}-\left(CH_2\right)_{n^2}-\underset{H}{N}-R^3 \qquad (1);$$

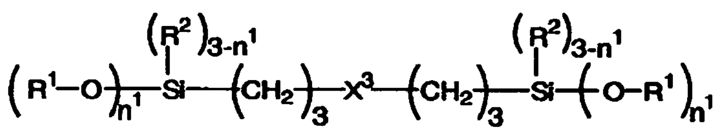


(2);



(3);

$(R^1\text{-}O)_3\text{-}Si\text{-}R^5$ (4); and



(5),

wherein R^1 represents a methyl group or an ethyl group;

R^2 represents a hydrogen atom, a methyl group or an ethyl group;

R^3 represents a hydrogen atom, a methyl group, an ethyl group, an ally group, a phenyl group or an organic group represented by the following general formula (6);

R^4 represents a methyl group, an ethyl group or a hydroxyethyl group;

R^5 represents a 3-(N-phenylamino)propyl group, a 3-(4,5-dihydroimidazolyl)propyl group or a 2-[N-(2-aminoethyl)aminomethyl phenyl]ethyl group;

X^1 represents a divalent alkylene having from 1 to 6 carbon atoms;

X^2 represents methylene which is a divalent organic group, oxygen or a secondary amine;

X^3 represents a divalent organic group represented by $-NH-$ or $-NHCH_2CH_2NH-$;

n^1 represents an integer of from 1 to 3;

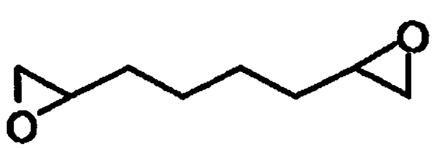
n^2 represents an integer of from 1 to 6; and

n^3 represents an integer of from 1 to 3:

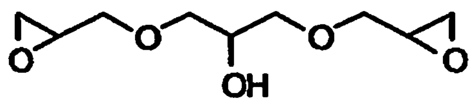
$$-\left(CH_2CH_2\text{-}\underset{H}{N}\right)_{n^4}-H \quad (6),$$

wherein n^4 represents an integer of from 0 to 2.

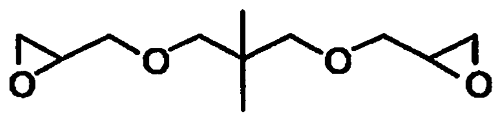
6. The production method as set forth in Claim 2, wherein the compound having at least 2 epoxy groups in a molecule is represented by the following general formulae (7) to (28):



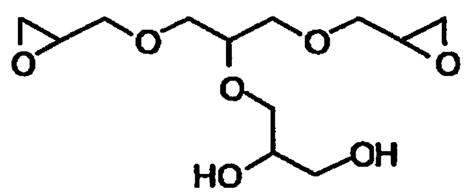
(7);



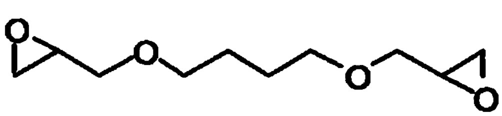
(8);



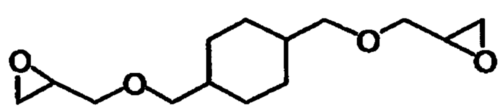
(9);



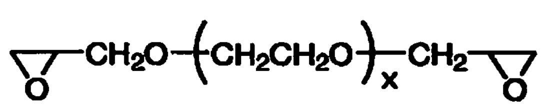
(10);



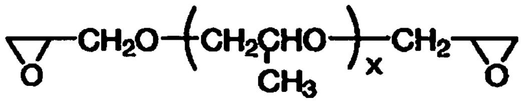
(11);



(12);

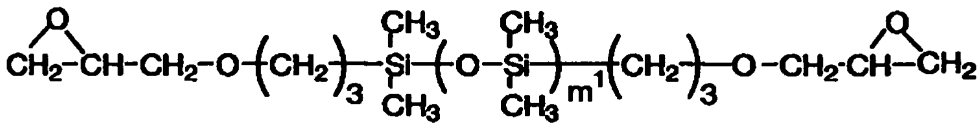


(13);



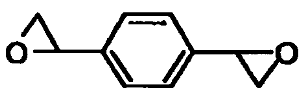
(14),

wherein x represents an integer of from 1 to 1000;

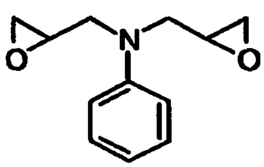


(15),

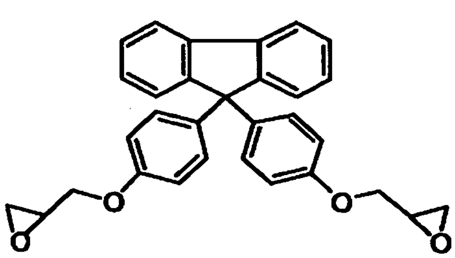
wherein m^1 represents an integer of from 1 to 100;



(16);

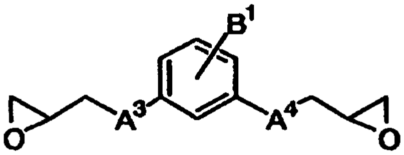


(17);



(18);

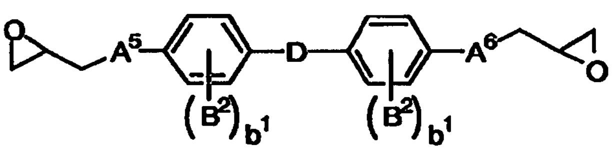
(19);



(20),

wherein A^1, A^2, A^3 and A^4 each independently represents a divalent linking group selected from among -O-, -C(=O)O-, -NHC(=O)O- and -OC(=O)O-; and

B^1 represents any one of substituents: -H, $-CH_3$ and $-OCH_3$;



(21),

wherein A^5 and A^6 each independently represent a divalent linking group selected from among -O-, -C(=O)O-, -NHC(=O)O- and -OC(=O)O- ;

B^2 represents any one of substituents: -H, $-CH_3$ and $-OCH_3$;

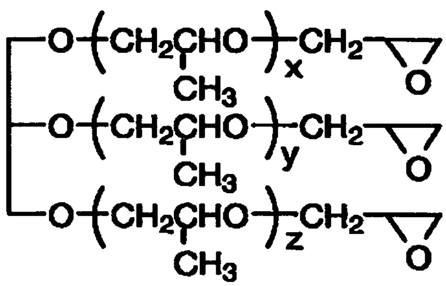
b^1 represents an integer of from 0 to 4;

D represents a single bond or any one of divalent linking groups: -O-, -C(=O)-, -C(=O)O-, -NHC(=O)-, -NH-, -N=N-, -CH=N-, -CH=CH-, -C(CN)=N-, -C≡C-, $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,

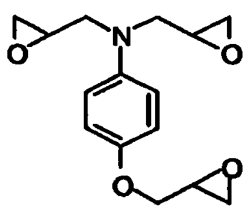
$-C(CH_3)_2-$ and the general formulae: $-O-(CH_2)_m-O-$ and $-O-(CH_2CH_2O)_n-$,

wherein m represents an integer of from 2 to 12; and

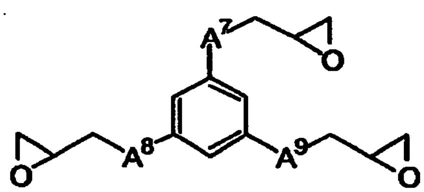
n represents an integer of from 1 to 5;



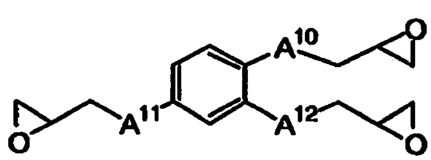
(22);



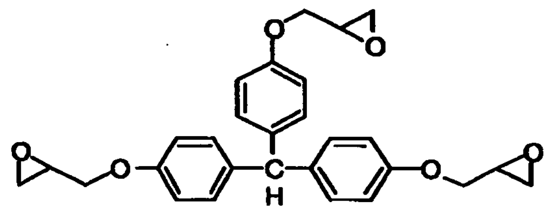
(23);



(24);



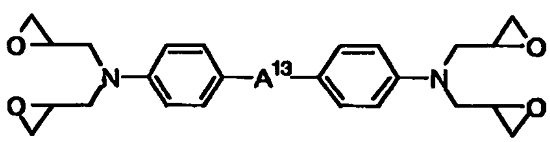
(25);

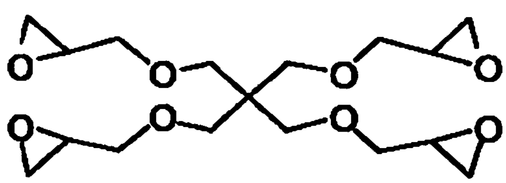

(26),

wherein x, y and z each independently represent an integer of from 1 to 20;

A^7, A^8 and A^9 each independently represents a divalent linking group selected from among -O-, -C(=O)O-, -NHC(=O)O-, and -OC(=O)O-; and

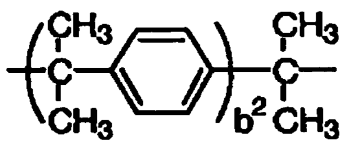
A^{10}, A^{11} and A^{12} each independently represents a divalent linking group selected from among -O-, -C(=O)O-, -NHC(=O)O- and -OC(=O)O-;


(27); and

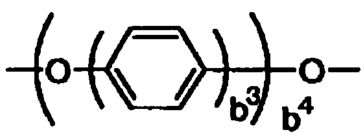

(28),

wherein A^{13} represents methylene or a linking group represented by any one of the following general formulae (29)

and (30):



(29); and



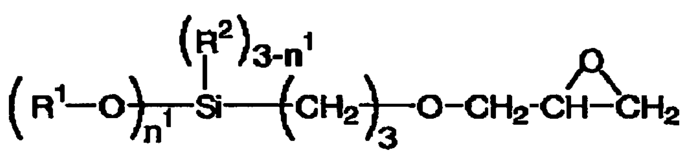
(30),

wherein b^2 represents an integer of from 0 to 4;

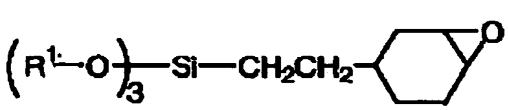
b^3 represents an integer of from 1 to 3; and

b^4 represents an integer of from 0 to 2.

7. The production method as set forth in Claim 3 or 4, wherein the alkoxysilane compound having an epoxy group is represented by the following general formula (31) or (32):



(31); or



(32),

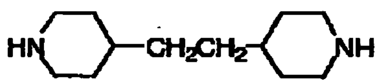
wherein R^1 and R^2 each independently represents a methyl

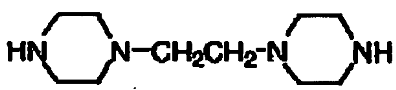
group or an ethyl group; and

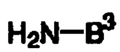
n^1 represents an integer of from 1 to 3.

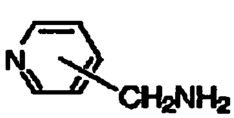
8. The production method as set forth in Claim 3, wherein the amine compound having at least 2 amine valences is represented by the following general formulae (33) to (51):


(33);


(34);

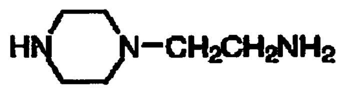

(35);

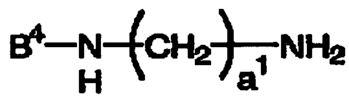

(36);

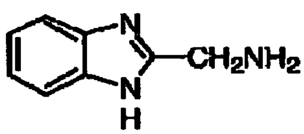

(37),

wherein B^3 represents a hydrocarbon group having from 2 to 18 carbon atoms or a group having at least one ether bond

in a hydrocarbon chain;

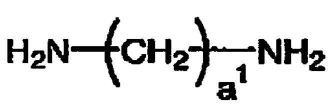

(38);

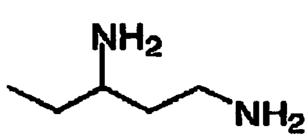

(39);

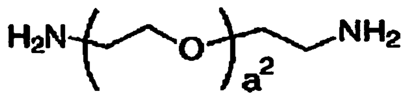

(40),

wherein a^1 represents an integer of from 2 to 18;

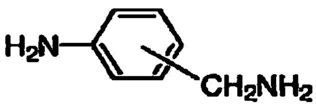
B^4 represents a hydrocarbon group having from 1 to 18 carbon atoms or a group having at least one ether bond in a hydrocarbon chain;


(41);

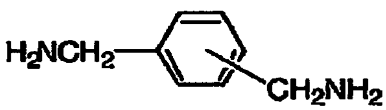

(42);



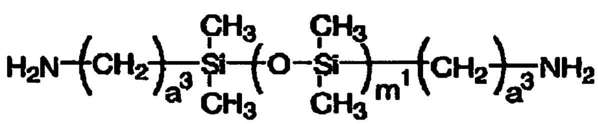
(43);



(44);



(45);



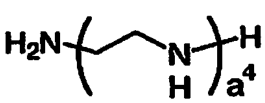
(46),

wherein a^1 represents an integer of from 2 to 18;

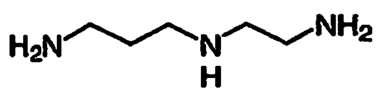
a^2 represents an integer of from 1 to 10000;

m^1 represents an integer of from 1 to 100; and

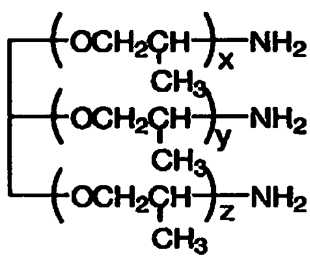
a^3 represents an integer of from 3 to 18;



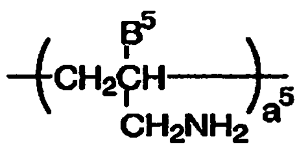
(47);



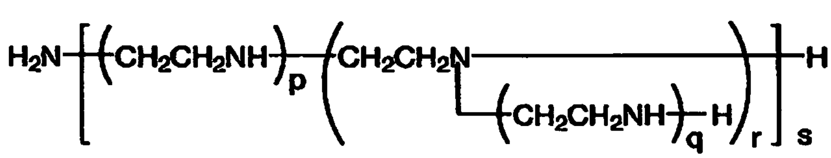
(48);



(49);



(50); and



(51),

wherein a^4 represents an integer of from 2 to 100;

x, y and z each independently represents an integer of from 1 to 20;

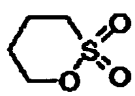
a^5 represents an integer of from 2 to 1000;

B^5 represents hydrogen or a methyl group; and

p, q, r and s each independently represents an integer of from 1 to 20.

9. The production method as set forth in any one of Claims 1 to 8, wherein the cyclic sultone is represented by the following general formula (52) or (53):

(52); or



(53).

10. The production method as set forth in any one of Claims 1 to 9, being characterized in that a condensation reaction of an alkoxysilane portion of the sulfonic acid derivative is progressed by a catalytic action of an self-sulfonic acid group of the sulfonic acid derivative generated by allowing to react with a cyclic sultone.

11. The production method as set forth in any one of Claims 1 to 10, being characterized in that the step for obtaining the sulfonic acid derivative and the condensation reaction step are simultaneously progressed.

12. The production method as set forth in any one of Claims 1 to 11, being characterized in that the condensation reaction step is performed in the presence of a metal alkoxide

having no reactivity with an epoxy group and an amino group.

13. The production method as set forth in Claim 12, wherein the metal alkoxide is represented by the following general formulae (54) to (61):

$$\left(R^1{-}O\right)_4{-}Si$$

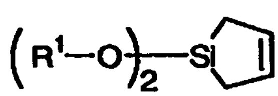
(54);

$$\left(R^1{-}O\right)_{n^1}{-}\underset{}{\overset{\left(R^2\right)_{3-n^1}}{\overset{|}{Si}}}{-}R^6$$

(55);

$$\left(R^1{-}O\right)_2{-}Si{-}\left(R^7\right)_2$$

(56);



(57);

$$\left(R^1{-}O\right)_{n^1}{-}\overset{\left(R^2\right)_{3-n^1}}{\overset{|}{Si}}{-}X^4{-}\overset{\left(R^2\right)_{3-n^1}}{\overset{|}{Si}}{-}\left(O{-}R^1\right)_{n^1}$$

(58);

$$\left(R^8-O\right)_4-Ti$$
(59);

$$\left(R^8-O\right)_4-Zr$$
(60); and

$$\left(R^8-O\right)_3-Al$$
(61),

wherein R^1 and R^2 each independently represents a methyl group or an ethyl group;

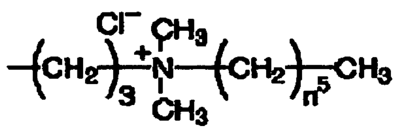
R^6 represents an alkyl group or alkenyl group having from 1 to 18 carbon atoms, a 2-cyanoethyl group, a 3-cyanopropyl group, a cyclohexyl group, a 2-(3-cyclohexenyl)ethyl group, a 3-cyclopentadienyl propyl group, a phenyl group, a toluyl group or a monovalent organic group having a quaternary ammonium group represented by the following general formula (62);

R^7 represents a cycloalkyl group or cycloalkenyl group having 5 or 6 carbon atoms;

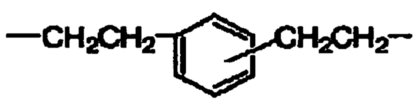
R^8 represents an alkyl group or alkenyl group having from 1 to 4 carbon atoms;

X^4 represents a single bond, oxygen, an alkylene group having from 1 to 9 carbon atoms, a vinylene group or a divalent organic group represented by the following general formula (63) to (65); and

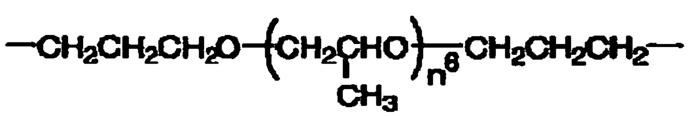
n^1 represents an integer of from 1 to 3:



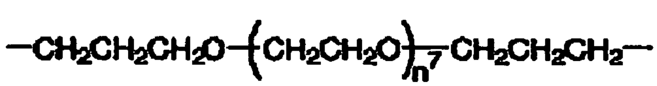
(62);



(63);



(64); and



(65),

wherein n^5 represents an integer of from 0 to 13;

n^6 represents an integer of from 1 to 10; and

n^7 represents an integer of from 0 to 20.

14. The production method as set forth in any one of

Claims 1 to 13, being characterized in that the condensation reaction step is performed in the presence of a metal oxide.

15. The production method as set forth in any one of Claims 1 to 14, being characterized in that the condensation reaction step is performed in the presence of an acid or an alkali.

16. The production method as set forth in any one of Claims 1 to 15, wherein the condensation reaction step is performed in an atmosphere of steam, an acidic or basic gas, and/or under a reduced pressure.

17. An organic-silica complex membrane, being obtained by the production method as set forth in any one of Claims 1 to 16.

18. A production method for an organic-silica complex membrane having a free sulfonic acid group in the complex membrane, being characterized in that the complex membrane as set forth in Claims 17 is dipped in a solvent containing an inorganic acid and/or an organic acid.

19. A production method for an organic-silica complex membrane having a free sulfonic acid group in the complex membrane, being characterized in that the complex membrane as set forth in Claim 17 is dipped in a solvent containing at least one type selected from the group consisting of: methyl sulfate, dimethyl sulfate, an alkyl halide having from 1 to 10 carbon atoms and an allyl halide having from 1 to 10 carbon atoms.

20. An organic-silica complex membrane, being obtained by the production method as set forth in Claim 18 or 19.

21. An electrolyte membrane, being characterized by comprising the organic-silica complex membrane as set forth in Claim 17 or 20.

22. An electrolyte membrane, being obtained by dipping the organic-silica complex membrane as set forth in Claim 17 or 20 in a solvent containing a lithium ion.

23. An electrochemical device, being characterized by comprising the electrolyte membrane as set forth in Claim 21 or 22.

24. A membrane transfer device, being characterized by comprising the organic-silica complex membrane as set forth in Claim 17 or 20.

25. A membrane reaction device, being characterized by comprising the organic-silica complex membrane as set forth in Claim 17 or 20.